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TRITIUM EFFECTS ON DYNAMIC MECHANICAL PROPERTIES OF POLYMERIC MATERIALS

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ABSTRACT

Dynamic mechanical analysis has been used to characterize the effects of tritium gas (initially 1 atm. pressure, ambient temperature) exposure over times up to 2.3 years on several thermoplastics- ultrahigh molecular weight polyethylene (UHMW-PE), polytetrafluoroethylene (PTFE), and Vespel® polyimide, and on several formulations of elastomers based on ethylene propylene diene monomer (EPDM). Tritium exposure stiffened the elastic modulus of UHMW-PE up to about 1 year and then softened it, and reduced the viscous response monotonically with time. PTFE initially stiffened, however the samples became too weak to handle after nine months exposure. The dynamic properties of Vespel® were not affected. The glass transition temperature of the EPDM formulations increased approximately 4° C. following three months tritium exposure.

INTRODUCTION

There are three known isotopes of hydrogen: "protium" (^{1}H), deuterium (^{2}H), and tritium (^{3}H). Tritium is radioactive, decaying by the beta decay mechanism with a Half-life of 12.3 years; the average decay energy is 5.7 KeV, and the maximum decay energy is 18.6 KeV [1]. Hydrogen molecules dissolve in and permeate polymeric materials [2], and so if tritium gas contacts structural polymers, tritium will likewise permeate the polymers. The radioactive decay of tritium results in a beta particle having a penetration depth of about 6 microns in matter of unit density and about 6 mm in air [3]. If solid polymers are exposed to tritium gas, the beta particles will impinge on the surface (directly from the gas) and also the bulk of the polymer will be exposed to beta radiation from decaying dissolved tritium molecules.

Polymers degrade when exposed to ionizing radiation [4, 5, 6]. The amount of degradation depends on many factors including polymer type, specific formulation, total dose, dose rate, and presence of oxygen. When polymers are exposed to ionizing radiation (gamma rays, alpha particles, or beta particles from tritium decay), highly reactive "free radical" groups form when the energy of the ionizing photon or particle is absorbed. These free radical groups continue to react in turn, in many complicated ways, and the initial overall response of any given polymer can be thought of as being either cross-linking or degradation by chain-scission. Materials

that cross-link initially become stiffer, stronger and less pliable and those that degrade initially become weaker and then finally decompose to a form that has no mechanical strength, such as a powder or a liquid. Some polymers undergo one dominant mode of degradation, while others exhibit a mixed mode of both cross-linking and chain-scission.

Many commercially available gas processing components (valves, seals, pumps, etc.) contain polymers; polymers are especially useful for reproducible seals such as valve stem tips and O-rings. Avoiding all polymers in tritium handling systems is thus economically impractical. There is a fairly large scientific literature about the relative resistance of polymers to gamma radiation in air, and to select polymers for tritium service it is assumed that the relative resistance of polymers to tritium is the same as that of the same polymers to gamma radiation in air. However, the service lifetime of a given polymeric component in a specific application currently can only be determined by monitoring the performance of the component.

To help understand the performance of polymers in tritium processing, a program is underway at the Savannah River Site to study effects of tritium gas exposure on the properties of several thermoplastics and elastomers. Materials used currently or historically at the Savannah River Site tritium facilities are chosen for study: three thermoplastics i) ultrahigh molecular weight polyethylene (UHMW-PE), ii) polytetrafluoroethylene (PTFE), and iii) Vespel® polyimide and four types of the elastomer ethylene propylene diene monomer (EPDM). Dynamic Mechanical Analysis (DMA) was used to evaluate the mechanical properties of the exposed polymer.

MATERIALS AND EXPOSURE CONDITIONS

UHMW-PE, PTFE, and Vespel® samples were cut from nominally 1.6 mm (1/16") thick sheet, to a size of about 30 mm by 10 mm. The PTFE was "virgin" unfilled, and the Vespel® was the SP-1 unfilled grade. The EPDM samples were obtained from Los Alamos National Laboratory (LANL): sheets of Nordel™ 1440 and Royalene® 580H, both standard graphite filled sheets from vendors and formulations synthesized without graphite at LANL were provided. The filled Nordel™ 1440 had a nominal thickness of 1.94 mm, the filled Royalene® 580 0.85 mm, the unfilled Nordel™ 0.7 mm and the unfilled Royalene® 0.65 mm. The filled polymers appeared black, and the unfilled versions appeared light grey. Rectangular slab-shaped samples having nominal lengths of 33 mm and nominal width of 9 mm were cut from the sheets.

The samples were exposed in closed stainless steel containers to what initially was 101 kPa (1 atmosphere) of pure tritium gas at ambient (room) temperature for various times, and the effects of tritium on the polymer samples was characterized by DMA.

DYNAMIC MECHANICAL ANALYSIS

A TA Instruments model 2980 dynamic mechanical analyzer was used for this study. This device applies a sinusoidal force at specified frequencies, and the resulting phase angle δ between the load and displacement is measured. From the measured load, displacement amplitude, phase angle and knowing the specimen geometry (rectangular slab used in this study) and sample holder type, the system calculates the various quantities that describe the elastic and viscoelastic properties. The modulus is represented as a complex number: the real part or "storage modulus" is a measure of the elastic deformation of the polymer, and the imaginary part or "loss modulus" measures the time-dependent viscoelastic deformation. Tan δ is the loss modulus divided by the storage modulus.

The sample configuration was the three-point bend configuration for the thermoplastics (ultrahigh molecular weight polyethylene (UHMW-PE), polytetrafluoroethylene (PTFE), and Vespel® polyimide) and single cantilever for the elastomer EPDM samples. The DMA controls the sinusoidal displacement amplitude, which is chosen to be within the region of linear viscoelasticity as determined in preliminary experiments that varied the amplitude. The force required to achieve the chosen amplitude and the phase angle between the applied force and the displacement of the sample, is measured continuously while the sample temperature is increased with time at 1° C/minute, and the device calculates the storage and loss moduli and tan δ for the chosen frequencies (1, 3, 10, 30 Hz) and temperature.

RESULTS

UHMW-PE

The loss modulus of unexposed UHMW-PE exhibits a pronounced maximum at 50° C. at 1 Hz (Fig. 1) that is reduced significantly after tritium exposure (Fig. 2). The tan delta of unexposed UHMW-PE increases significantly starting at room temperature to the softening point (Fig. 1), and this increase is eliminated from the tritium exposed material (Fig. 2).

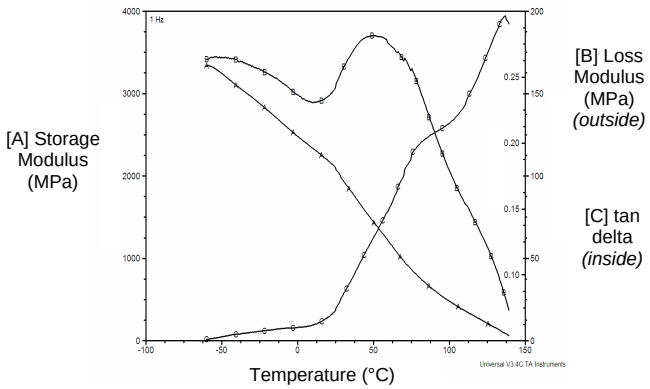

Figure 1: Storage modulus [A], loss modulus [B] and tan delta [C] of unexposed UHMW-PE. 1 Hz. test frequency, temperature initially at -60° C. and increased at 1° C./min. [7]

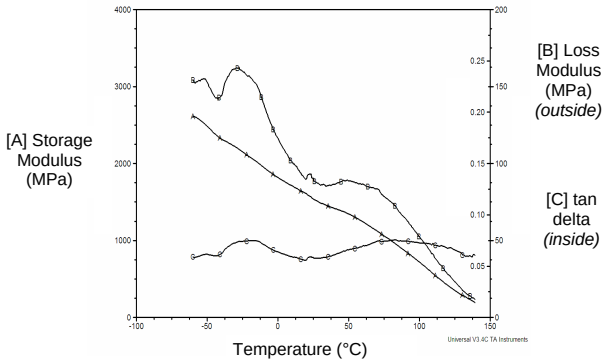

Figure 2: Storage modulus [A], loss modulus [B] and tan delta [C] of UHMW-PE after 2.3 years tritium exposure. 1 Hz. Temperature set at -60° C. and increased at 1° C./min. [7].

The storage modulus of UHMW-PE initially increases with the length of tritium exposure, and then decreases (Fig. 3). This observation is in accord with the classical concept of initial stiffening by radiation induced cross-linking, followed by a net degradation of properties.

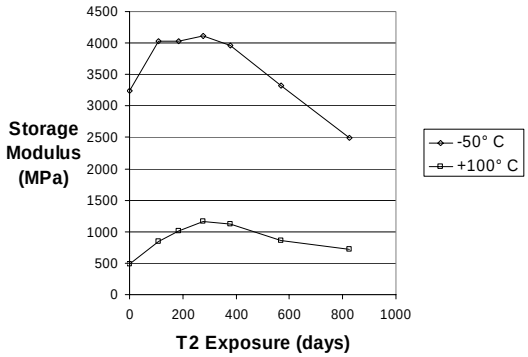

Figure 3. Variation of storage modulus of UHMW-PE with exposure time, at -50° and +100° C. as indicated. 1Hz [7].

At 100° C. there is a significant increase in the storage modulus with test frequency of unexposed UHMW-PE, and tritium exposure decreases this significantly (Fig. 4).

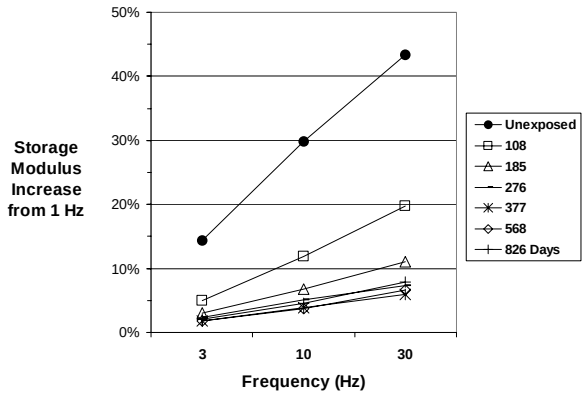

Figure 4: Storage modulus of UHMW-PE at 3, 10 and 30 Hz divided by that at 1 Hz, for various lengths of tritium exposure (0-826 days as indicated)[7]. Temperature 100° C.

PTFE

The storage modulus, loss modulus, and tan delta of PTFE reveal a crystallographic phase transition at about 30° C. (Fig. 5) [8]. This feature is independent of test frequency (1, 3, 10, 30 Hz).

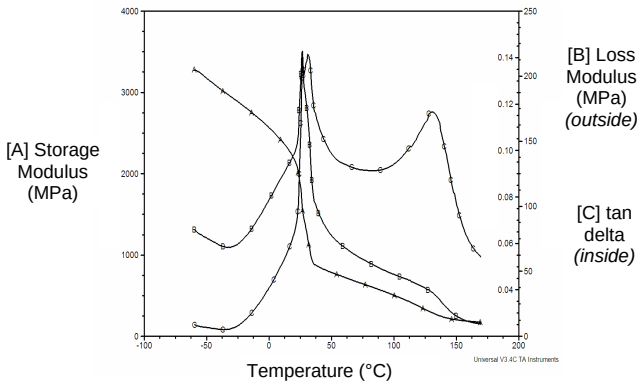

Figure 5. Storage modulus [A], loss modulus [B], and tan delta [C] of unexposed PTFE. 1 Hz applied load, 1° C./min temperature rise. [7]

The crystallographic phase transition does not change with tritium exposure; however the tan delta peak between 100-160° C. is reduced similarly to UHMW-PE (Fig. 6).

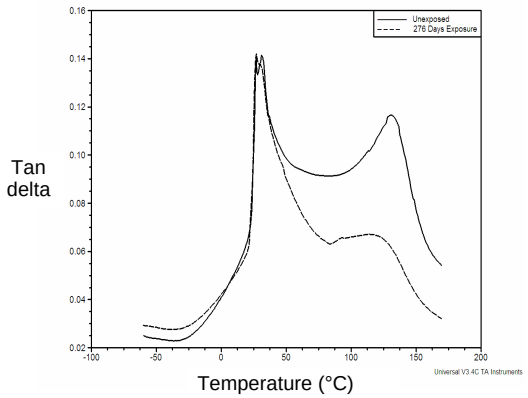

Figure 6. Tan delta versus temperature for PTFE, unexposed (solid line) and 276 days exposure to tritium gas (dotted line)[7]

PTFE samples exposed to tritium for longer than 276 days were too weak to handle without breaking. Up to 276 days exposure, the storage modulus increased and the frequency dependence of the storage modulus decreased similar to UHMW-PE.

Vespel® polyimide

The viscoelastic response of Vespel® SP-1 polyimide (Fig. 7) was unaffected by tritium exposure of up to 2.3 years.

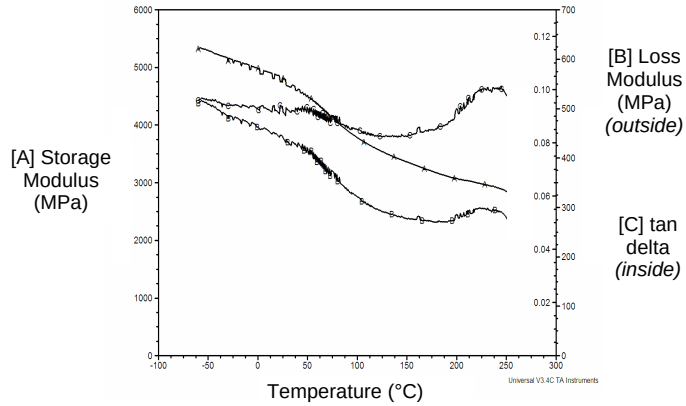

Figure 7. Storage modulus (A), loss modulus (B), tan delta (C) of unexposed Vespel® SP-1 polyimide. 1 Hz applied load, 1° C./min temperature rise.[7]

EPDM

ASTM E 1640 "Standard Test Method for Assignment of the Glass Transition Temperature by Dynamic Mechanical Analysis" uses the intersection of two tangents of the storage modulus versus temperature curve: the tangent of data below Tg and the tangent at the inflection point of the modulus in the middle of the glass transition (Fig. 8). The temperature of the tangents intersection is regarded as being Tg. The standard requires an applied frequency of 1 Hz and a temperature increase rate of 1 °C/minute, which were used for these tests. Another method for determining Tg is the peak temperature of the loss modulus (Fig. 8).

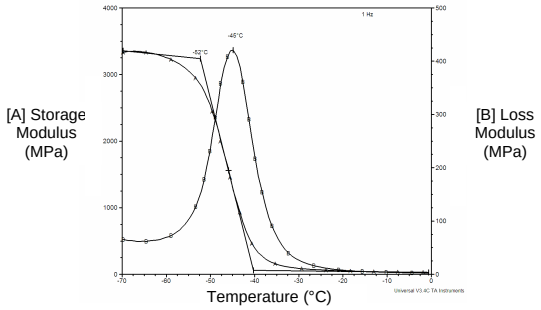

Figure 8. Storage Modulus (A) and Loss Modulus (B) of one-week exposed filled Nordel® 1440 at 1 Hz, temperature increasing 1° C./min. Tangent intercept method of ASTM E-1640 giving Tg= -52° C. and loss modulus peak temperature Tg = -45° C. is shown.

A plot of the measured glass transition temperatures reveals that three months of tritium exposure results in about a 3° C. increase in Tg (Fig. 9) for all four resins tested. There was no difference comparing the filled versus unfilled material, and the

Royalene® resins had a uniformly lower Tg than that for the comparable Nordel® resins (Fig. 9)

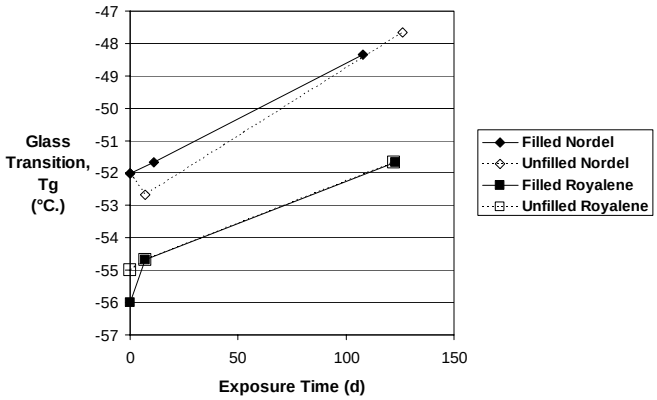

Figure 9. Glass transition temperature (Tg ° C.) versus tritium exposure time. (Tg determined using the ASTM E-1640 tangent intercept method.

CONCLUSIONS

Tritium gas exposure reduces the viscoelastic response of UHMW-PE and PTFE. The exposure initially increases the storage modulus for both, and for UHMW-PE eventually the storage modulus decreases. This behavior is consistent with the degradation of polymers by other types of ionizing radiation. The glass transition temperature of several EPDM formulations increases with tritium gas exposure.

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REFERENCES

1. DOE Handbook: Tritium Handling and Safe Storage. US Department of Energy Handbook, Appendix A, DOE-HDBK 1129-2007 (2007). URL: http://www.hss.energy.gov/NuclearSafety/techstds/standard/hdbk1129/hdbk1129-07.pdf

2. S. Pauly, “Permeability and Diffusion Data”, chapter in J. Brandrup, E.H. Immergut, E.A. Grulke, eds. Polymer Handbook (Fourth Edition). Wiley-Interscience (New York 1999), pp. 543-569.

3. E.A. Evans, Tritium and its Compounds. D. Van Nostrand (Princeton, New Jersey USA 1966), p. 2.

4. D.C. Phillips. “Effects of Radiation on Polymers”. *Materials Science and Technology*, Vol. 4 (January 1988), pp 85-91.

5. A. Chapiro. Radiation Chemistry of Polymeric Systems. Vol. XV of series High Polymers, Wiley-Interscience (New York 1962), Chapter IX.

6. W.W. Parkinson, O. Sisman. “The Use of Plastics and Elastomers in Nuclear Radiation”. *Nuclear Engineering and Design*, vol. 17 (1971), pp 247-280.

7. E.A. Clark, K. L. Shanahan, “Effects of Tritium on UHMW-PE, PTFE, and Vespel® polyimide”, *Fusion Science and Technology*, 52 (2007), pp 1007-1011.

8. P. J. Rae, E. N. Brown, “The Properties of Poly(tetrafluoroethylene) (PTFE) in Tension”. *Polymer*, 46 (2005), p. 8128.